Ionic Self Assembled Monolayer (ISAM) Processes for Electronic Materials and Devices

Scientific and Technical Report

Reporting Period: 1 October 1997 to 31 October 1997

BMDO SBIR Phase I Contract No. N00014-97C-0233

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1.0 Executive Summary

The objective of this 6-month BMDO Phase I SBIR program is to develop electronic and optoelectronic device products based on nanoparticle self-assembly methods, and to develop the plan for their commercialization for military and commercial applications.

F&S is using novel ionic self-assembled monolayer (ISAM) processes for the fabrication of both active electronic materials and passive conducting interconnect materials. In combination, such materials may be used to synthesize submicron-scale, low-power microelectronic, optoelectronic and physical transducer devices for use in military and consumer communication, instrumentation and display systems. The ISAM technique offers very low manufacturing costs, advantages of processing at ambient temperature and pressure, and functional tailoring of materials response through the selective incorporation of electronic, optical, magnetic, dielectric, ferroelectric, electrostrictive and other molecules into each of the layers of the self-assembled thin-films.

Accomplishments during the sixth month of this program (October 1 – October 31, 1997) include the following items. These items are summarized in this report.

- Obtained additional information concerning ISAM/nanoparticle electronic and optoelectronic material and device requirements
- Developed processing methods to improve ISAM thin-film material properties
- Extended characterization of platinum nanoparticles
- Improved the PPV (poly(phenylene vinylene)) conjugation process
- <u>Demonstrated the operation of an ISAM optical fiber polarizer; this is the primary accomplishment of the reporting period</u>
- Enhanced $\chi^{(2)}$ response of ISAM thin-films using novel polymer dyes
- Demonstrated ISAM thin-film patterning
- Extended plan for device commercialization, in part with larger companies

This program parallels another separate BMDO Phase I program in which F&S is using ISAM processes to develop nanoparticle-based protective coatings for space-based and other military systems. Dr. John Pazik at ONR is the monitor of that program. Although these programs are directed at totally different applications and commercial markets, they overlap in the need to develop (1) conductive multi-layer thin-films to serve as both EMI shielding layers and patterned electronic interconnects, and (2) active electro-optic materials that can be used both in microdevices and as active coatings. Both BMDO programs build on prior F&S and Virginia Tech work with ARO (Dr. Robert Reeber) and Virginia Tech DURIP program support from ARO (Dr. John Prater).

2.0 Project Task Review

The technical tasks proposed by F&S as key to the development and commercialization of ISAM-processed electronic and optoelectronic devices are summarized as follows.

Task 1 - Review performance metrics of space-based and commercial electronics that may be achieved using polymer/nanoparticle ISAM thin-film processing. Determine quantitative requirements on passive properties such as electrical conductivity and shielding, and active device characteristics including power and current per element, spatial resolution, transient response and field tuning possibilities.

Task 2 - Consider the material functions required to achieve device performance metrics established above. Determine how patterned electrical, electronic, optical, magnetic, mechanical and other properties will satisfy these requirements.

Task 3 - Develop precursor aqueous solution chemistries required to obtain uniform suspensions of desired anions and cations in solution. This is based on recent exciting results with inorganic particles including TiO_2, Fe_3O_4 and ZrO_2 and poly(*p*-phenylenevinylene) (PPV) precursors for self-assembled LEDs.

Task 4 - Design, fabricate and characterize ISAM-based EMI-shielding coatings for space-based, other DoD and commercial electronic packaging applications by incorporating conducting nanoparticles and chiral molecules in each nanolayer. This builds directly on prior Virginia Tech research of Fe_3O_4 ISAM thin-films.

Task 5 - Design, fabricate and characterize ISAM-based patterned conductive interconnects for lightweight and low-volume electronic devices and systems.

Task 6 - Design, fabricate and characterize ISAM-based nanostructured electronic and optoelectronic devices. During the last two months of this program, F&S has made substantial progress in this area.

Task 7 - Develop the plan for upscaling ISAM device production volume and the accompanying business plan for commercialization and marketing. Litton is directly assisting F&S with this task.

This report briefly describes progress made on each of these tasks during the final month of the program.

3.0 Task Schedule

Monthly work schedule goals are outlined in Table 3-1. The most important completed results of work in each month are as follows.

<u>COMPLETED</u>

May	• demonstration of ISAM conductive and EO thin-film synthesis
June	• demonstration of initial electro-optic modulator and optical fiber polarizer prototypes
July	• demonstration of patterned ISAM conductive interconnects
	• synthesis of PPV precursors for self-assembled LEDs
August	• demonstration of ISAM LED and *p-n* semiconductor materials
September	• analysis of ISAM-processed *p-n* semiconductor device
October	• completion of ISAM material and device commercialization plan

The project is on schedule as of 31 October 1997.

ID	Task Name	Duration	Start
1	Set Device Metrics	27.2w	Thu 5/1/97
2	ID Nanoparticle Functions	81d	Thu 5/1/97
3	Conductive	47d	Thu 5/1/97
4	Semiconducting	56d	Tue 5/20/97
5	Electro-Optic	46d	Sun 6/15/97
6	Develop ISAM Precursors	89d	Sun 6/1/97
7	Conductive	46d	Sun 6/1/97
8	Semiconducting	9.2w	Sun 6/15/97
9	Electro-Optic	66d	Tue 7/1/97
10	EMI Coatings	71d	Thu 5/15/97
11	Deposit Coatings	48d	Thu 5/15/97
12	Characterize	57d	Sun 6/1/97
13	Demonstrate Interconnects	101d	Sun 6/15/97
14	Deposit Thin-Films	23d	Sun 6/15/97
15	Pattern/Characterize	90d	Mon 6/30/97
16	Demonstrate Devices	119d	Sun 5/25/97
17	Electro-Optic	96d	Sun 5/25/97
18	Fiber Optic	89d	Sun 6/15/97
19	pn Devices	71d	Fri 7/25/97
20	Other	56d	Fri 8/15/97
21	Commercialization Plan	27.2w	Thu 5/1/97

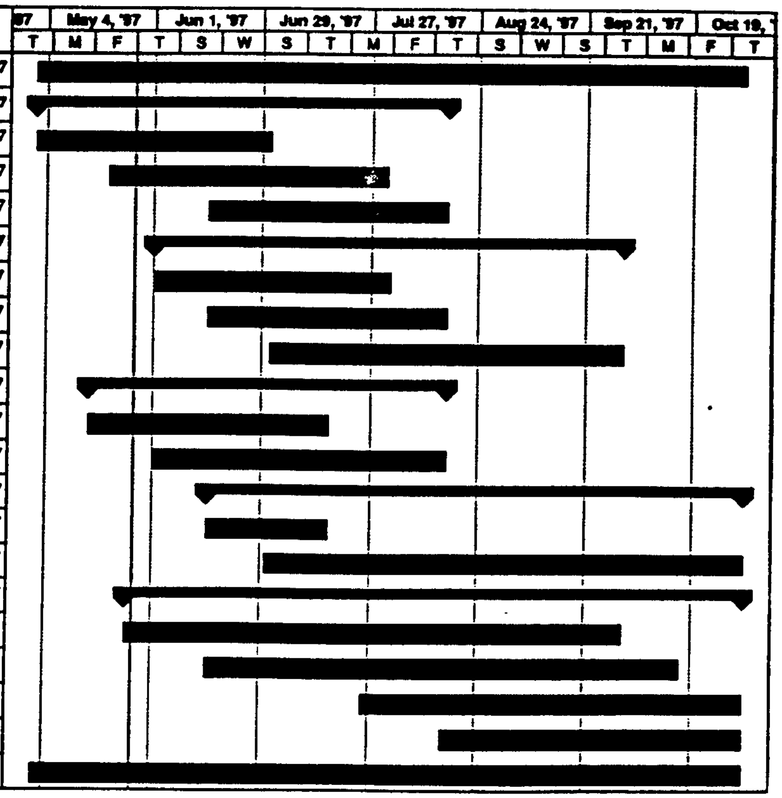


Table 3-1 Primary BMDO Phase I Monthly Work Schedule Goals.

4.0 Review of Accomplishments During Period 1 October – 31 October 1997

This section briefly reviews accomplishments during final month of the six-month BMDO Phase I SBIR project and summarizes accomplishments of the previous five months.

4.1 Requirements for ISAM Electronic and Optoelectronic Devices

Determining and updating requirements for inorganic/organic nanoparticle/polymer-based microelectronic and optoelectronic materials and devices has been performed extensively during the entire 6-month Phase I program. A large number of government laboratory and industrial scientists and engineers have been consulted by telephone and by personal visits, and many have visited either FEORC or F&S to discuss technical developments and methods of cooperation.

Government agency staff contacted and briefed concerning this program have included researchers and program managers at BMDO, DARPA, ONR, AFOSR, ARO, NRL, NRaD, Wright Laboratory, Phillips Laboratory, NIST, NSF and NAWC. Company researchers briefed include individuals at Litton, IDA, Lockheed-Martin Astronautics, Lockheed-Martin Research Laboratories, Northrop-Grumman, Boeing, TACAN, GE, 3M, Alcatel, Lucent and other companies.

During the last month of the program, the following additional efforts were made to more clearly define active device material requirements for BMDO, other DoD and commercial applications.

- Extended literature survey to determine how to best approach Phase II process development and prototype product demonstration tasks.
- Visited by Tycho Submarine Systems (formerly AT&T Submarine Systems) research director on 2 October to discuss possible ISAM-based devices for use in undersea optical fiber transmission systems.
- Telephone discussions with 3M research staff (R. Claus) concerning successful ISAM-based optical fiber polarizer demonstration. F&S worked with 3M on a prior program to consider metal-coated fiber, and discussed fiber polarizer and related products as part of that program.
- Visited by ETA Inc. president and staff on 13 October to discuss possible use of light emitting device arrays on eyewear for corrective eye diagnostics and treatment.
- Visited (R. Claus) Newport News Shipbuilding on 22 October to discuss possibility of ISAM-fabricated displays for submarine and commercial double-hulled ship instrumentation systems.
- Visited (R. Claus) NASA-LaRC Materials Division (Dr. Terry St. Clair, Dr. Joycelyn Simpson) on 28-30 October, in part to discuss potential use of NASA-LaRC high T_g polymers in ISAM processing for multiple applications.
- Discussions between Dr. R. Claus and Dr. Janet Sater, IDA, at NASA-LaRC, concerning program progress and proposed Phase II commercialization plans.

Note that all expenses for travel to visit individuals and conferences during this program have been provided through cost sharing by both Fiber Core Technologies (FCT) and Virginia Tech,

and through other funds from F&S, and not by Phase I SBIR project funds. Additional commercialization support from FCT is summarized below.

Continued analysis and discussion with these and other individuals and groups indicates that the following materials are required in order to synthesize polymer-based electronic and optoelectronic devices for both DoD and consumer products.

1. Patterned conducting contacts, with acceptably high conductivity or with proper work function and ohmic and rectifying characteristics with respect to active device material(s). In some cases, such as space-based multifunctional structures, flexible conducting interconnects are desired on low-weight, mechanically elastic polymer substrates.
2. Electron and hole transport materials with mobilities that are suitably high and that can be designed and fabricated through practical materials processing. Again, fabrication on flexible substrates may be desired.
3. Recombination and charge separation/scavenging region materials, again with properties that may be designed and controlled through processing.
4. Large electrical conductivity and permeability of packaging layers to allow effective electromagnetic interference (EMI) shielding.
5. Electric field-tunable dielectric properties, for applications in discrete microwave electronic devices and waveguide structures.
6. Electro-optic, ferroelectric, nonlinear optical (NLO) and related properties related to the lack of a center of inversion at the macroscopic level.
7. Robust materials with resistance to changes in properties caused by thermal or mechanical stress.

Additional potential requirements that may be allowed by nanoparticle thin-films and required by specific product targets are discussed in sections below that consider particular materials and device applications.

4.2 Developments in Nanoparticle, Precursor and Thin-Film Synthesis

During this Phase I program, F&S made substantial progress in the development of methods for 1) the controlled chemical-based synthesis of nanoparticle inorganic oxides, noble metals, and organic polymer-based LED precursors, 2) the formation of ionic aqueous solutions from these nanoparticles, and 3) their incorporation via self-assembly into functional thin-films and first-generation devices. The characteristics, performance and functionality of nanoparticle-based self-assembled electronic and optoelectronic device products depend critically on the species of nanoparticles, and their mean size, size distribution, and relative spatial orientation in the self-assembled thin-films. This section briefly outlines F&S' progress in each of these areas.

Accomplishments during the first five months of this program (May 1 – September 30, 1997) include the following items that are summarized in the three previous reports.

- Synthesized and characterized Fe_3O_4 nanoparticle/polymer coatings
- Synthesized ZrO_2, Pt and Au nanoparticles and electro-optic dye ionic solutions

- Characterized n-type TiO_2 nanoparticle quantum size effects
- Synthesized and characterized ISAM thin-films of n-type semiconductor TiO_2 nanoparticle/polymer multilayers
- Synthesized ISAM thin-films of electro-optical particle/polymer multilayers, using electro-optical dye materials
- Synthesized poly(1,4-phenylenevinylene) (PPV) anionic and cationic precursor solutions; synthesized and characterized ionic self-assembled PPV thin-films
- Synthesized polyhydroxylated fullerene derivative
- Synthesized sulfonic acid ring substituted polyaniline
- Synthesized and characterized ionic self-assembled gold nanoparticle thin-films
- Investigated the incorporation of metallic nanoparticles into thin-film monolayers for property modification and enhancement
- Investigated the modification of solution salt concentration to control the thickness of each bilayer

During the last month of the program, the following additional progress was made toward the synthesis and analysis of novel nanoparticle solutions and thin-films.

4.2.1 Developments in the Synthesis of Water-Soluble Conducting Polymers

Several nanoparticle/polymer thin-film systems have been considered for the implementation of conducting coatings during the Phase I program. Results for nanoparticle metal oxide/polymer multilayer thin-films have been discussed in prior reports.

During the last month of the program, additional work has been performed to synthesize polyaniline precursors which will allow the ISAM fabrication of conducting polymer thin-films, of use for both conducting and EMI shielding as well as device interconnects. Difficulties have been encountered in the formation of homogeneous thin-films from the water soluble forms of polyaniline synthesized. We suspect that these difficulties are due to suboptimal combinations of concentration and pH, and are in the process of a parametric study of fabrication conditions to optimize material properties. The optimization of both the polyaniline precursor and ISAM processing will form two important tasks of the Phase II effort to be proposed to BMDO.

4.2.2 Improvements to ISAM Processing

Using the ionic precursor solutions described above, we have investigated the incorporation of metallic nanoparticles into intermediate monolayers to enhance properties through controlled energy state coupling and resonance methods. This energy state enhancement is critically dependent on nanoparticle size and species and tuning of these properties could enable improved design of the conductivity, charge generation and separation, charge transfer, optical generation, and other properties in fabricated thin-film layers.

In an effort to model this effect, platinum nanoparticles in solution were analyzed using the zeta potential system. The smallest particle size measurable in the Zetasizer 3000 system is 1.0 nm. 90% of the platinum nanoparticles were less than 1.3 nm, with a mean zeta potential of 37.2 mV. The zeta potential distribution is shown below in Figure 4-1. Zeta potential is the potential

which is often most important in governing charge mediated particle interactions and thus the behavior of a suspension.

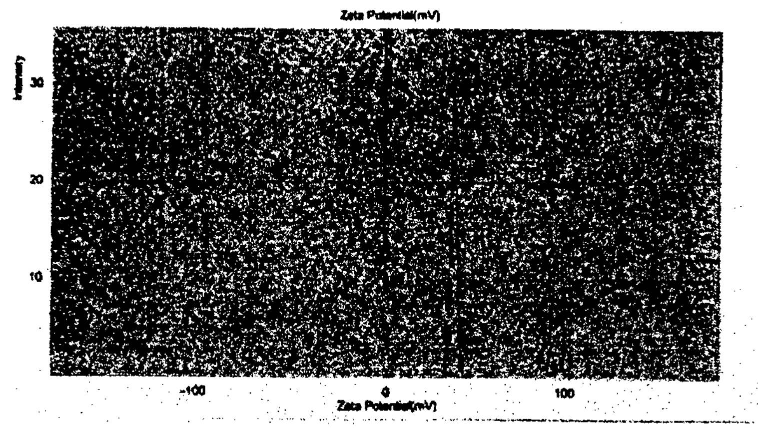


Figure 4-1. Zeta Potential Distribution of Platinum Nanoparticle Solution.

4.3 Development of Self-Assembled PPV-Based LEDs

Polymer light emitting diodes (LEDs) and other light-emitting devices have attracted both scientific and business attention recently due to potential applications in low-cost and flexible personal display devices and related instrumentation systems. F&S has considered ways to enter the polymer display device market, based on its patent position in the area of self-assembled organic/inorganic thin-films. During the Phase I program period, we have made progress in the following areas.

- Synthesized poly(1,4-phenylenevinylene) (PPV) anionic and cationic precursor solutions
- Ionically self-assembled and characterized PPV thin-films
- Demonstrated initial electrode pattering on prototype ISAM thin-film devices
- Optimized the PPV (poly(phenylene vinylene)) thermal conjugation process
- Designed, fabricated and characterized PPV LED prototype devices
- Demonstrated diode emission from a prototype ISAM PPV-based LED

4.3.1 Synthesis of PPV Precursor Solutions

PPV anionic and cationic precursor solutions were synthesized to allow the ISAM self-assembly of prototype LED thin-films on ITO-coated glass substrates. PPV exhibits an extremely high electrical conductivity (10^5 S/cm) with good optical characteristics. The synthesis of the PPV precursor is illustrated in Figure 4-2.

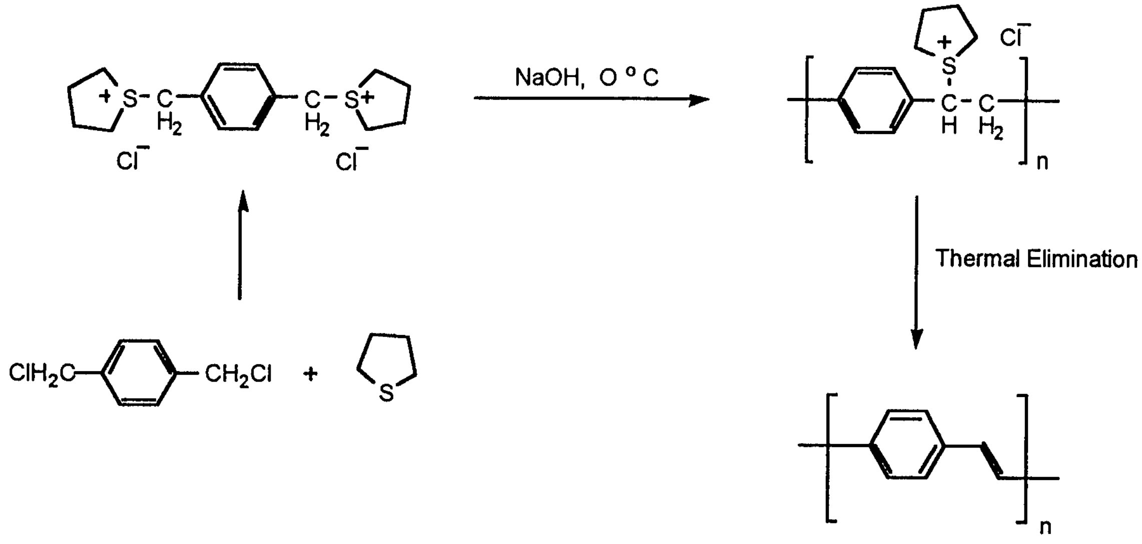
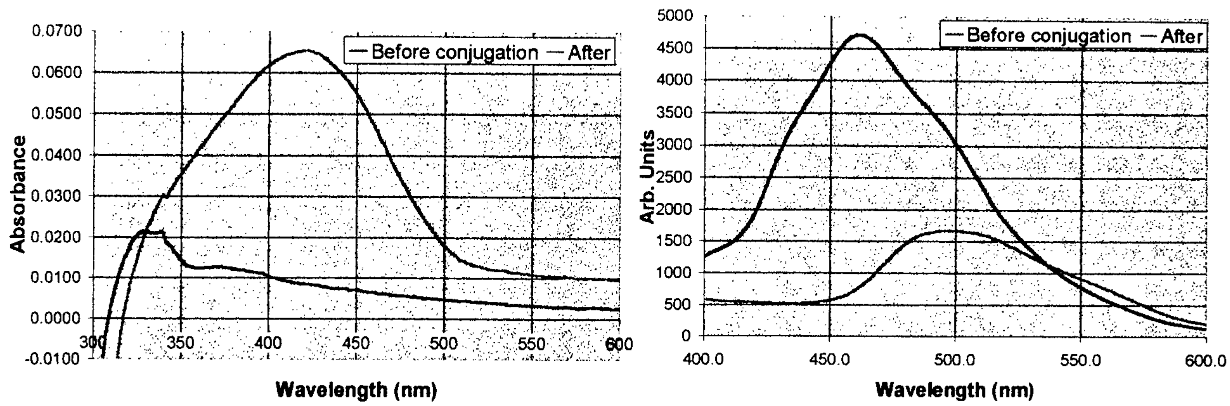


Figure 4-2. F&S PPV LED Precursor Synthesis Method.

4.3.2 Optimization of PPV Conjugation Process

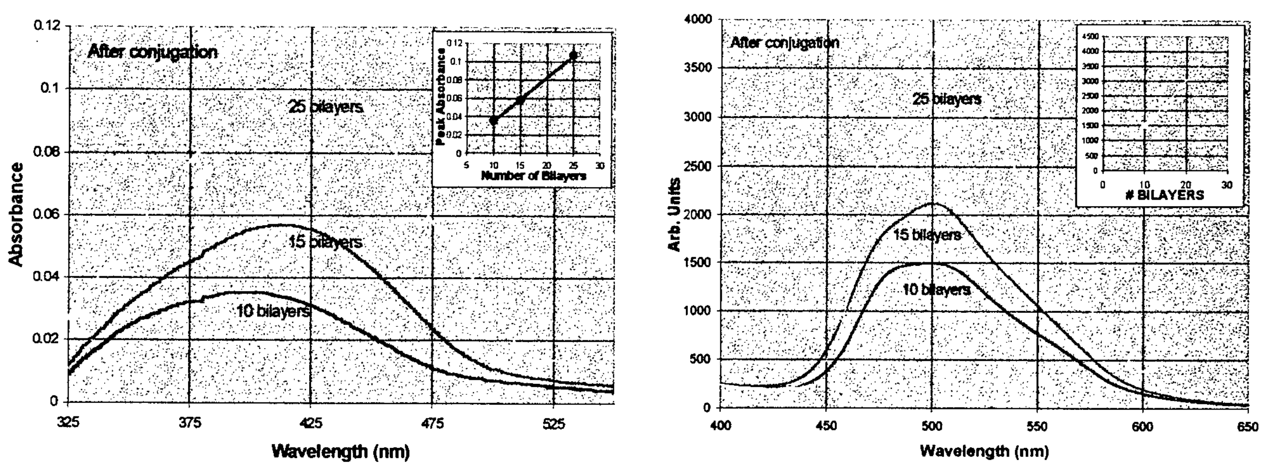
PPV thin film samples with varying numbers of bilayers were self-assembled on ITO-coated glass substrates and allowed to thermally conjugate in the vacuum oven for predetermined lengths of time. Conversion of the thin film color from clear to green and changes in the UV-Vis absorption and fluorescence spectrum verify conjugation of the PPV thin films. A distinct decrease was evident in the main fluorescence peak after conjugation, while UV-Vis spectra show the growth of an absorbance peak around 380 nm after conjugation, which agrees with literature [12]. The magnitude of change in absorption and fluorescence spectra as well as film color increase with increased conjugation time. Experimental results showed that 2-3 day conjugation resulted in the most desirable absorbance and fluorescence characteristics. Figures 4-3(a) and (b) are representative UV-Vis absorbance and fluorescence spectra of 15 bilayer PPV thin film coatings on ITO-coated glass substrates before and after a 3-day thermal conjugation period.

Figure 4-4 (a) and (b) compare UV-Vis absorbance and fluorescence spectra for PPV thin films with different numbers of bilayers on ITO-coated glass substrates after conjugation for 55 hrs. The linear increase in absorbance and fluorescence with the addition of each bilayer is illustrated by the inset of Figure 4-4. Each of the UV-Vis and fluorescence spectroscopy data curves shown is the average of at least three sets of data obtained at different locations on the specimen. The maximum differences between data at different locations is at most several percent, indicating excellent uniformity of the films.



(a) (b)

Figure 4-3. (a) UV-vis Absorbance (b) Fluorescence of a 15 Bilayer PPV Thin-Film Before and After 3 Day Conjugation.



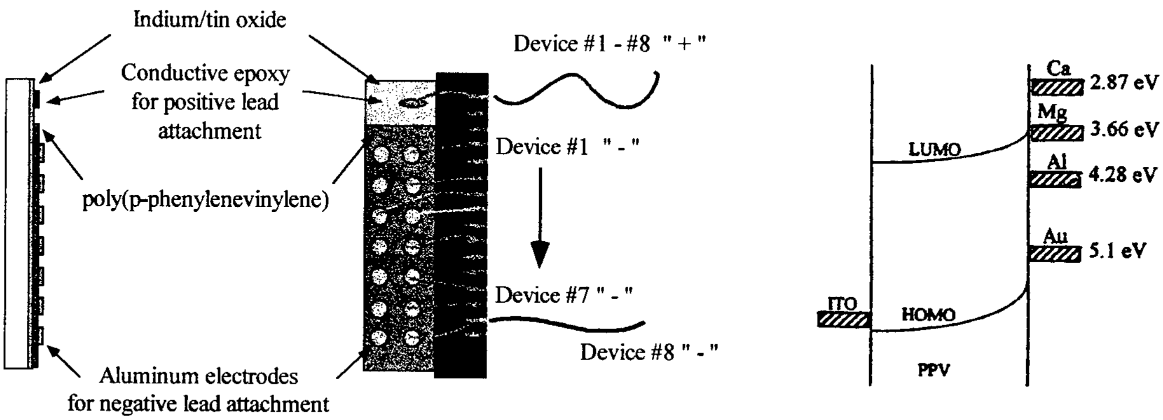
(a) (b)

Figure 4-4. UV-Vis (a) and Fluorescence (b) of PPV Thin-Films with Different Numbers of Bilayers.

4.3.3 Fabrication and Connectorization of LED Sample

Electroluminescence from conjugated polymers has been considered for more than ten years [5-7], and spin-coated PPV has been demonstrated as the single semiconductor layer between metallic electrodes in prototype LEDs. PPV has an energy gap between π and π^* states of about 2.5 eV, and produces luminescence in a band below this energy, as shown in Figure 4-4. The flexibility in both material and device design allowed by multi-layer PPV device ISAM self-assembly rather than "bulk" spin coating, is the basis of F&S' approach to LED and other device fabrication and commercialization.

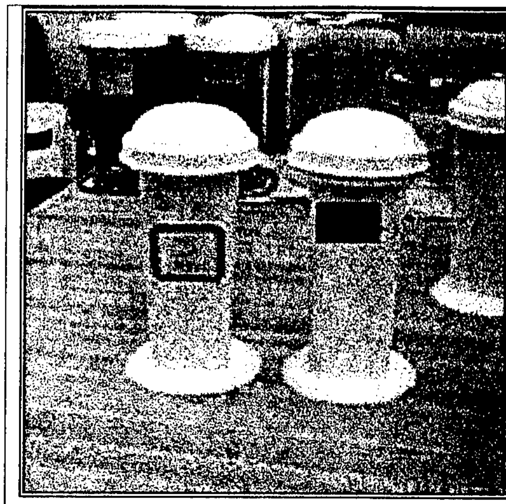
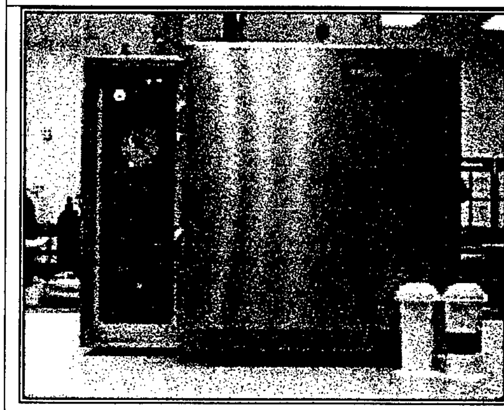
Light generation in a polymer LED requires a series of steps, which include charge injection, transport, electron-hole capture, and radiative decay of the exciton thus produced. Injection and transport of holes from the positive electrode into the bulk of the polymer multi-layer thin-film must be matched by injection and transport of electrons from the opposite electrode [6]. Injection of charges from most electrode materials requires that charges surmount or tunnel through a barrier at the interface. This is expected on examination of the positions of the electrode metal work functions and the positions of the π HOMO and π^* LUMO of the polymer. For the case of PPV, ITO provides a relatively good match for hole injection, although there is a barrier of about 0.2 eV; we have thus chosen ITO-coated glass substrates for initial work. Electron injection is more difficult without the use of low work function metals such as calcium or magnesium (see in Figure 4-5). We have reviewed much prior work concerning the mechanism for charge injection into the polymer layer [5, and references therein], and have chosen aluminum as an easily evaporated top electrode layer material for first demonstrations. Recent devices have been fabricated with magnesium electrodes, but characterization has not been completed.

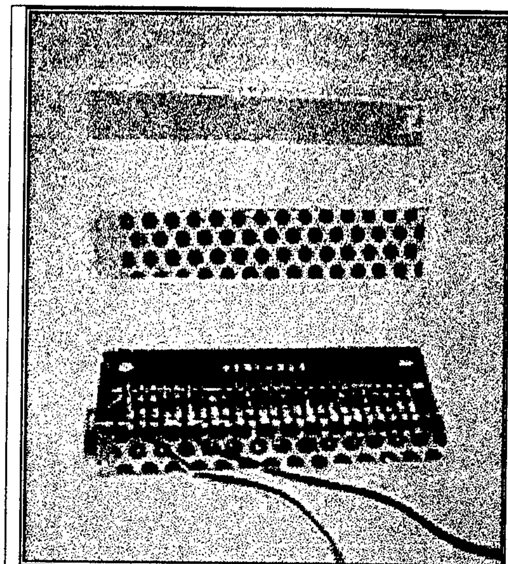


(a) (b)

Figure 4-5. (a) Schematic of Initial PPV-based LED Design (b) Band Structure Under Forward Bias with Fermi Energies Shown for Electrode Metals with Respect to the π Highest Occupied Molecular Orbitals (HOMOs) and the π^* Lowest Unoccupied Molecular Orbitals (LUMOs).

The initial prototype design for a self-assembled, single semiconducting layer PPV LED requires deposition of electrodes on the conjugated PPV thin films as illustrated in Figure 4-5. Using an Auto306 Edwards high vacuum deposition system, illustrated in Figure 4-6, approximately 1000 Å of aluminum was deposited onto the PPV. To ensure a high level of cleanliness, the deposition system was allowed to pump down to base pressures in the 10^{-7} Torr range. Through masking techniques, a single PPV film sample resulted in 8 to 10 actual separate LED devices on each substrate. This allowed for easy probing during I-V curve tracing and photodetection described in section 4.3.4. After the aluminum electrodes were deposited on the PPV sample, connectorization was accomplished with wire leads and conductive epoxy. The epoxy enables lead attachment during characterization of the LED. Figure 4-6 illustrates simplified steps for prototype LED device fabrication.

 PMA/PPV Precursor Polyelectrolyte Solutions for Self Assembly of Thin-Films.	**Step 1:** Ionic self-assembly of PPV/PMA thin-film on ITO-coated glass.
 Vacuum Oven Used for PPV Conjugation Process.	**Step 2:** Thermal conjugation of PPV films in a vacuum oven at 207 °C for 55 hours.
 Auto 306 Edwards Evaporation System	**Step 3:** Deposition of a grid of aluminum electrodes by evaporation.



(a) Conjugated PPV Thin-Film on ITO-coated Glass.
(b) PPV Film with Aluminum Electrodes Deposited.
(c) Prototype PPV LED With Leads Attached.

Step 4: Connectorization through wire leads and conductive epoxy.

Figure 4-6. Prototype LED Fabrication.

During the initial testing, it became evident that some problems must be overcome for efficient LED operation. One was the deterioration of the deposited aluminum contacts, resulting in damaged LED devices. The device degradation was attributed to oxidation of the aluminum electrodes or damage during lead attachment of the device. Secondary gold coatings were investigated in an effort to reduce oxidation problems or damage of the aluminum contacts during lead attachment. In addition, magnesium coatings were deposited since Mg has a more suitable work function (see Figure 4-5) and should be a more efficient charge injecting electrode coating. Figure 4-7 is a photograph of different prototype LED devices fabricated for characterization during this Phase I program. Additional modifications to the prototype LED device will be investigated in Phase II. The self-assembly of PPV film itself is currently under improvement, and we are considering the possibility of a different functional material in order to improve the carrier transition in the active media and the recombination probability in the emission area.

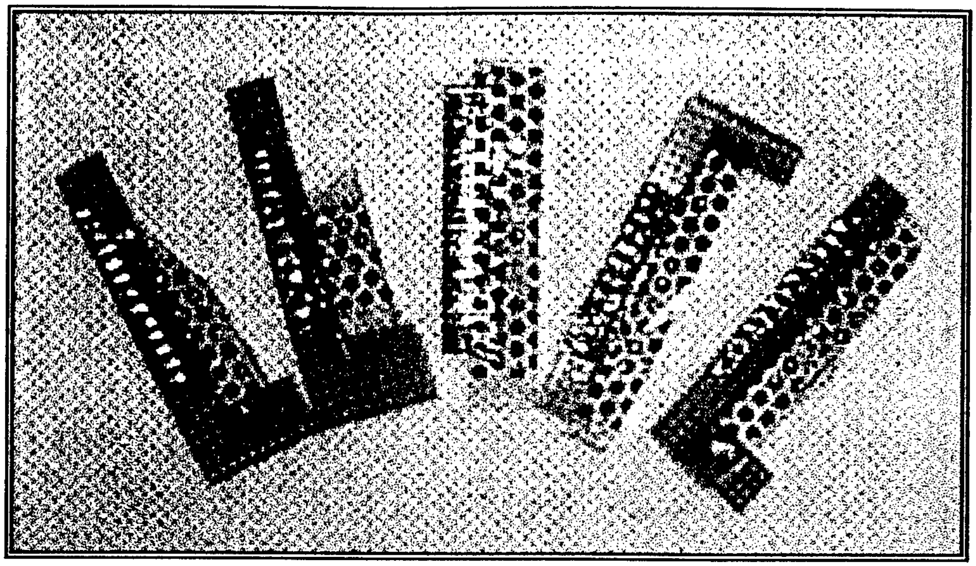


Figure 4-7. Prototype LED Devices.

4.3.4 Experimental Set-up for LED Characterization

Characterization of PPV LED devices included I-V curve tracing the samples to obtain required activation voltages, followed by actual photodetection experiments. Figure 4-8 and 4-9 are a schematic and photographs of the I-V curve tracing set-up. The LED device was placed in a sample holder and connected to a function generator through a resistive network with the positive lead attached to the uncoated ITO-glass substrate and the negative lead attached to the aluminum electrode as illustrated in Figure 4-5. The resistive network was designed to remove any possible transients or spikes generated from the power supply. A digital oscilloscope was used to capture the I-V curve trace of each device. Representative I-V curves for various pixels from an initial prototype LED device with 15 bilayers are illustrated in Figure 4-10.

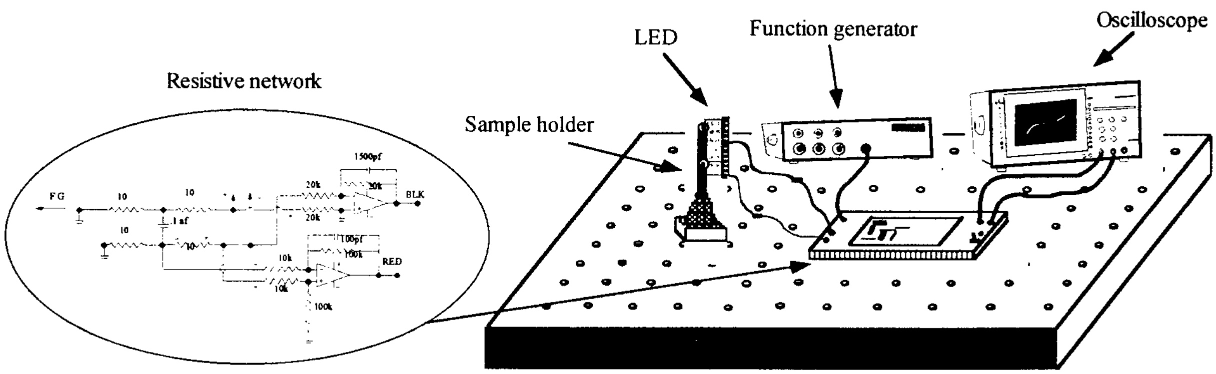


Figure 4-8. Schematic of LED I-V Curve Tracing Set-up.

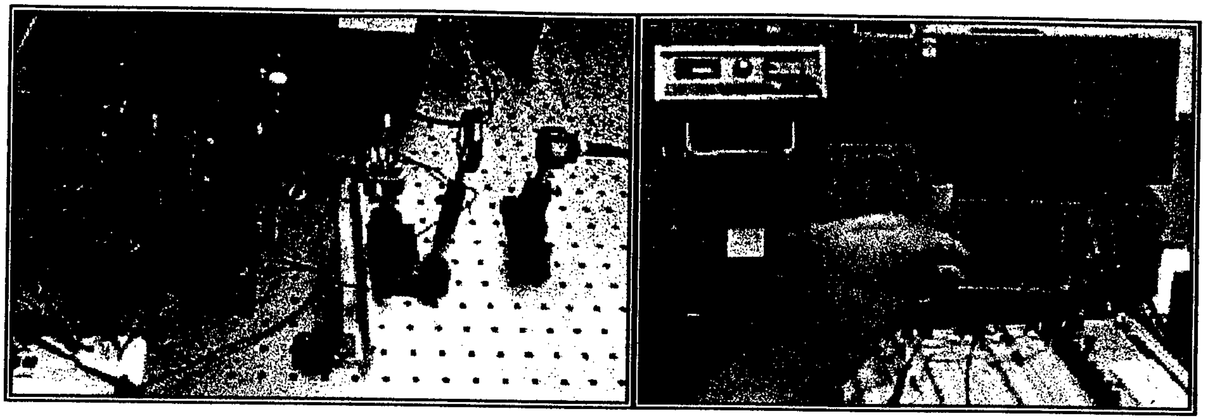


Figure 4-9. Photograph of LED I-V Curve Tracing Set-up.

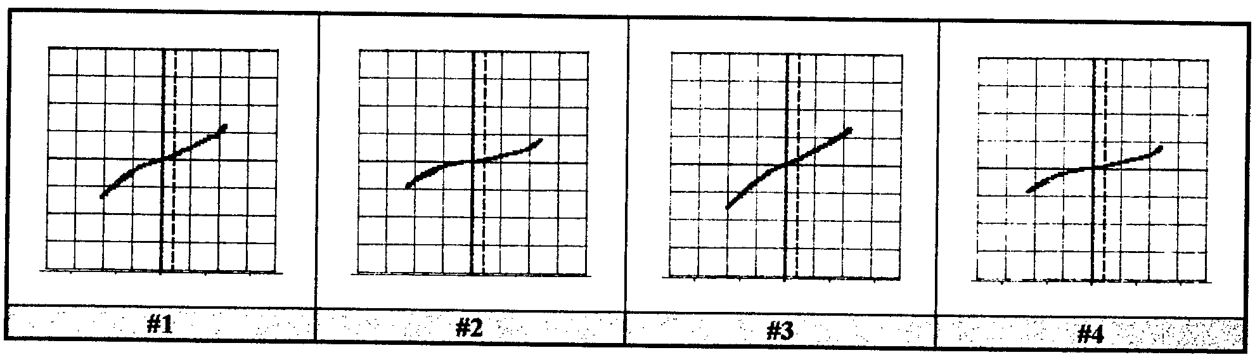
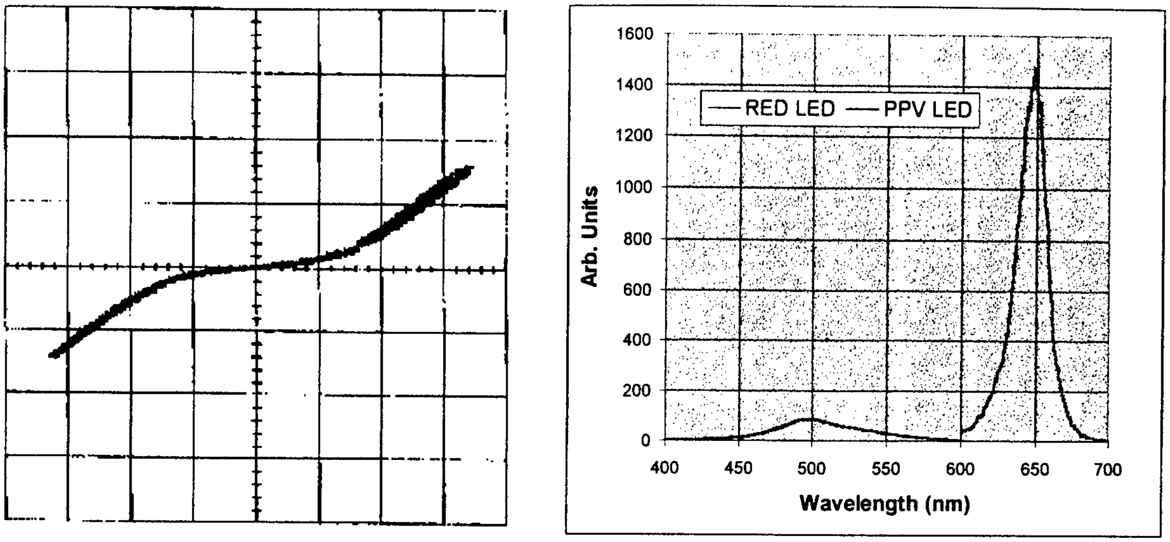


Figure 4-10. I-V Curves for Various Pixels from Initial Prototype LED Device.

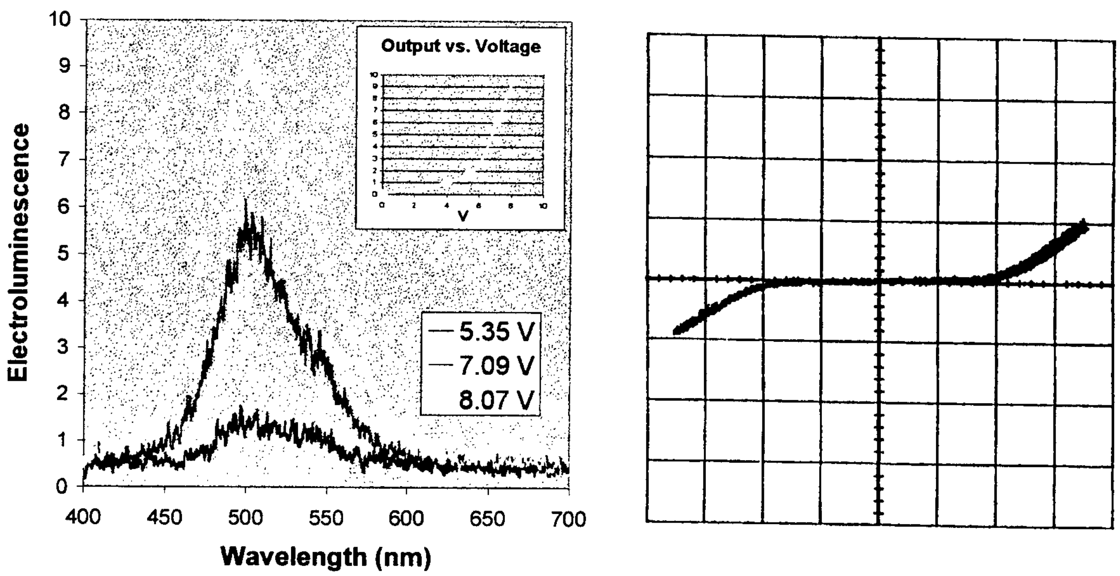
Figure 4-11a is an I-V curve measured from a selected pixel on one of the protoype LED devices. From this curve a forward bias and current of 7.5 Volts/ 38 mA was chosen to drive the LED device. Figure 4-11b is the plot of output light obtained using a highly sensitive fluorescence spectrophotometer for detection. The plot indicates a photon emission from the device when driven at 7.5 Volts compared to the 0 Volt base line. A commercially available red LED was used to calibrate the photon emission from the prototype. The output of the red LED at a specific driving voltage was approximately 1.5 nW. During Phase II, steps will be taken to increase the efficiency of the PPV-based LED devices.



(a) (b)

Figure 4-11. (a) I-V Characteristic Curve for Device (20/mA/div, 2V/Div) (b) Fluorescence Plot Indicating Photon Emission from Protoype LED Device with Commercial Red LED Comparison.

Similar fluorescence data is shown in Figure 4-12a, which indicates photon emission from a prototype LED device for various voltage settings. The inset gives a characteristic intensity vs. voltage plot for the LED. Appropriate driving current was determines from the I/V characteristic shown in Figure 4-12b.



(a) (b)

Figure 4-12. (a)Fluorescence Plot Indicating Photon Emission from Protoype LED Device For Various Voltage Settings, (b) I/V Characteristic for Prototype LED Device (20/mA/div, 2V/Div).

During Phase II, other possible polymer materials, electrode materials and improved device fabrication processes will be investigated to optimize the efficiency of ISAM polymer-based LED devices.

4.4 Demonstration of SPR Effect and Optical Fiber Polarizer

Previously during this Phase I SBIR, F&S demonstrated self-assembled coatings for optical fiber polarizers. The operation of the fiber polarizer is based on the principle of surface plasmon resonance (SPR). Surface plasmon theory states that when a wave travels at the boundary between two materials with different refractive indices, the input is absorbed at a specific angle.

The fiber polarizer shown in Figure 4-13 was constructed using 1300 nm single mode optical fiber which was mounted on a piece of polymer and polished until the cladding was removed and the core was exposed on one face of the fiber. The polishing instrument is shown in Figure 4-14. A thin layer (100 A^{o}) of gold was sputtered onto the polished surface of the fiber and an iron oxide/polymer coating was self-assembled over the gold. Polarization measurements were taken after each bilayer. The analyzer angle versus the intensity of the light output of the polarizer were plotted for 1, 5 and 23 bilayers in Figure 4-15. For comparison, the same plot is shown for a commercially available fiber polarizer in Figure 4-16. The difference between the highest intensity and the lowest intensity output increased with the number of the bilayers. This reached a peak value after 23 bilayers and then dropped with additional bilayers. A log plot of this result is shown in Figure 4-17. The polarization effect of the fiber with the coating is evident.

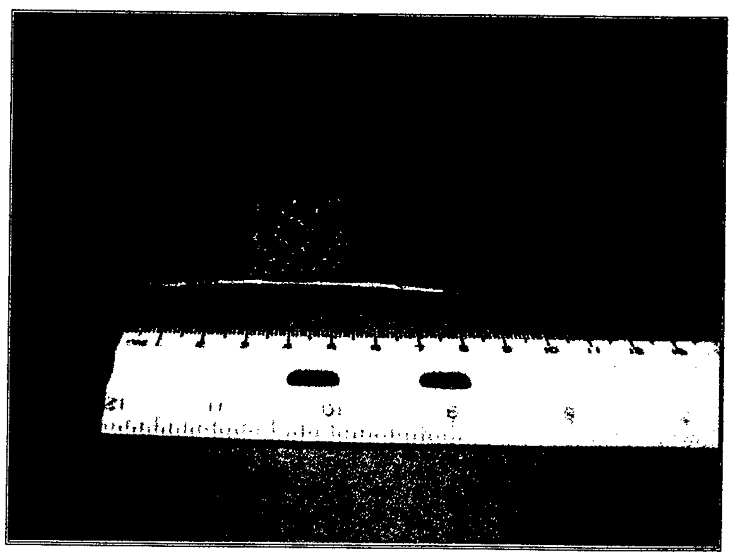


Figure 4-13. Optical Fiber Polarizer.

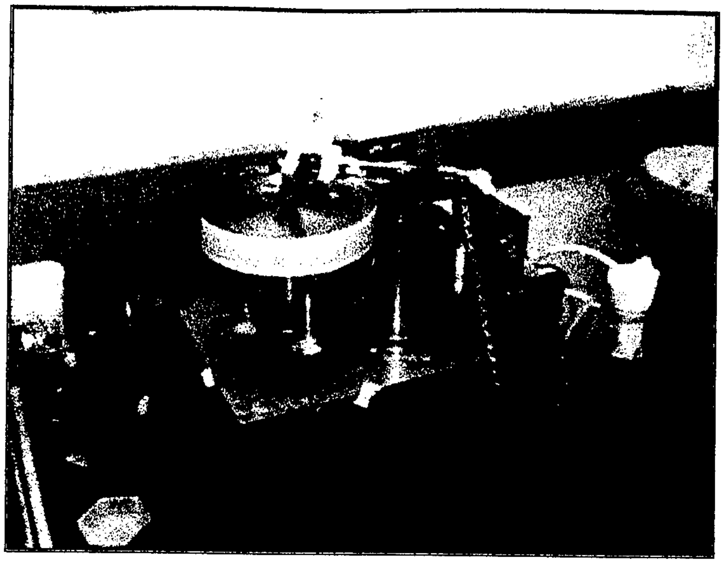


Figure 4-14. Polisher.

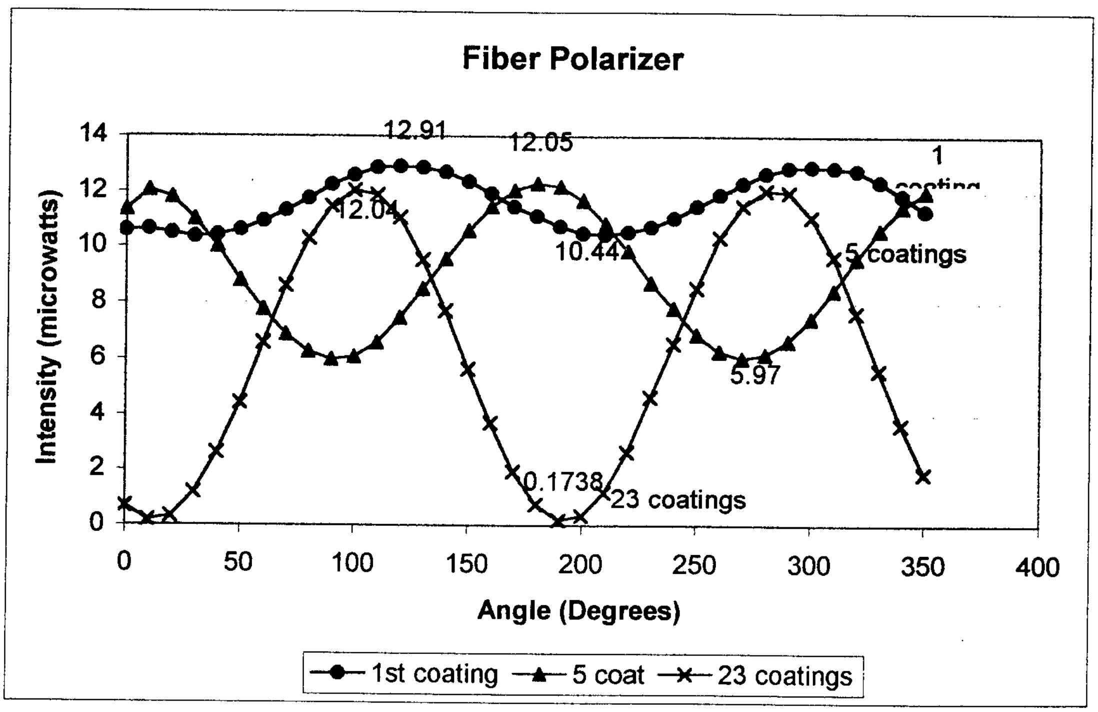


Figure 4-15. Angle versus Output Intensity for Fiber Polarizer.

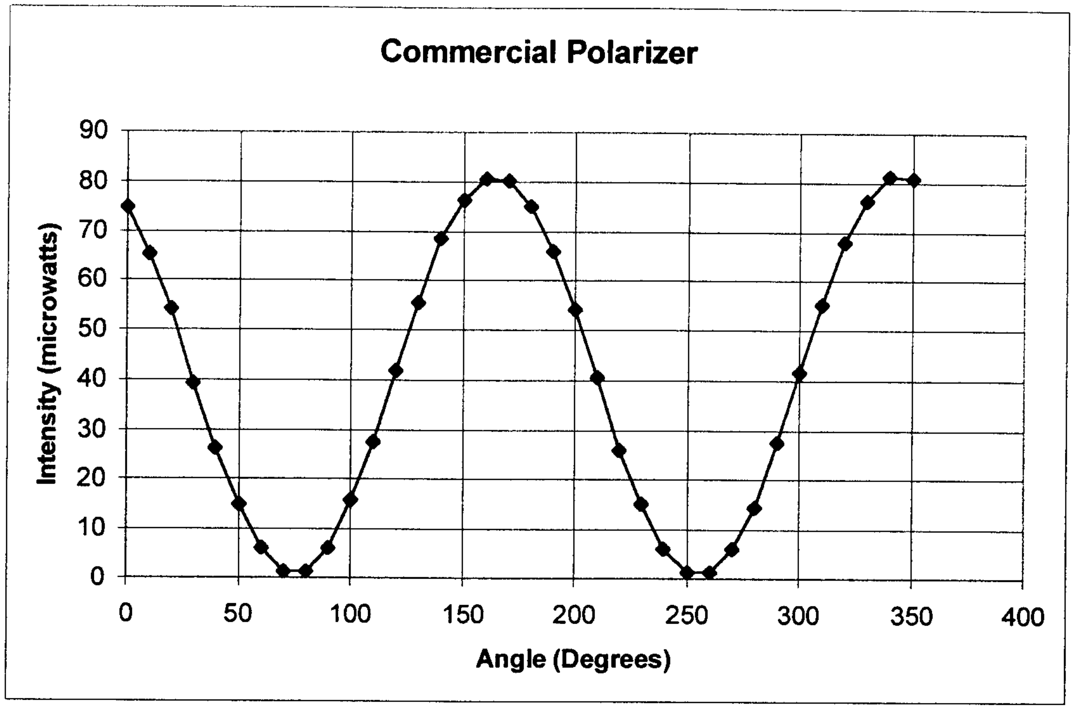


Figure 4-16. Angle versus Output Intensity for Commercial Polarizer.

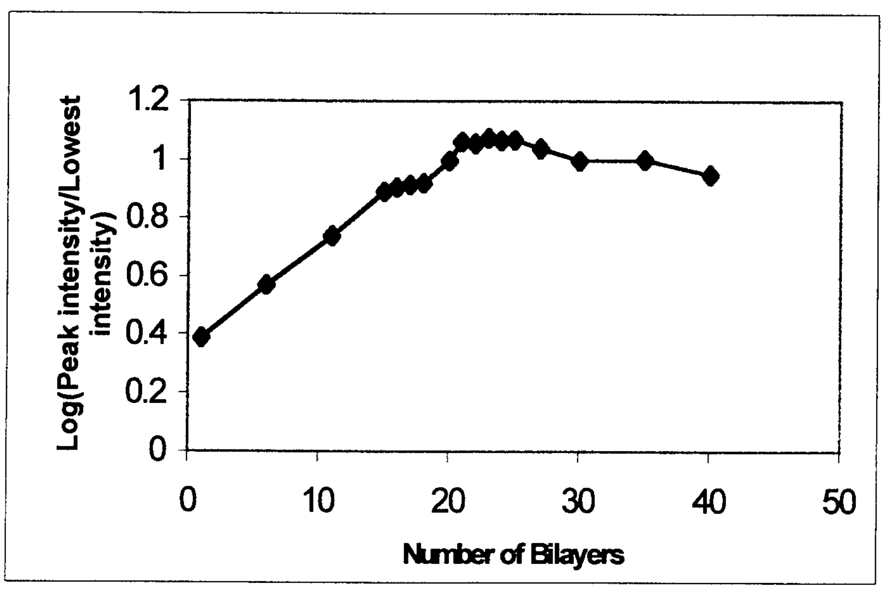


Figure 4-17. Difference Between Peak and Minimum Intensity vs. Number of Bilayers.

By using different species of nanoparticles and altering the bilayer thickness for better control at the peak polarization, further improvements can be made in the optical fiber polarizer.

4.5 Demonstration of Additional NLO Materials Response

Accomplishments in this area discussed in previous reports include the following.

- Measured $\chi^{(2)}$ electro-optic coefficients of noncentrosymmetric ISAM coatings
- Demonstrated $\chi^{(2)}$ NLO response in additional polar self-assembled thin-films
- Synthesized polyhydroxylated fullerene derivative
- Investigated grating growth in ionic self-assembled thin-films

In first three months of the current program, we reported the initial observation of nonlinear optical (NLO) behavior in polymer/organic dye ISAM thin-films, using commercially available dye molecules, P-S119 and poly{1-[4-(3-carboxy-4-hydroxyphenylaxo)benzensulfo-namido]-1,2-ethanediyl, sodium salt) (PCBS, from Aldrich).

The polar ordering of molecules that occurs due to the inherent nature of the ISAM process suggests that a number of similar NLO thin-films may be synthesized using both other standard chromophore dyes and molecules specifically designed to yield an enhanced macro-scale net dipole moment. During this reporting period, we have demonstrated similar NLO performance in a thin-film of novel polyanions, Polydye 1 and Polydye 2, which were synthesized by the research team. Again, the polymer dye acts as the active polyanion layer with polydiallyl-dimethylammonium chloride (PDDA) as the passive polycation layer.

The second harmonic generation results are shown in Figures 4-19 And 4-20. Polydye 1 exhibited a 600% increase in $\chi^{(2)}$ over P-S119 (see Figure 4-18); Polydye 2 also shows an increase, but is still on the same order of magnitude as the commercially available dye.

Such NLO materials may be used in electro-optic signal modulation and processing devices, and, perhaps with modification, optical limiting components.

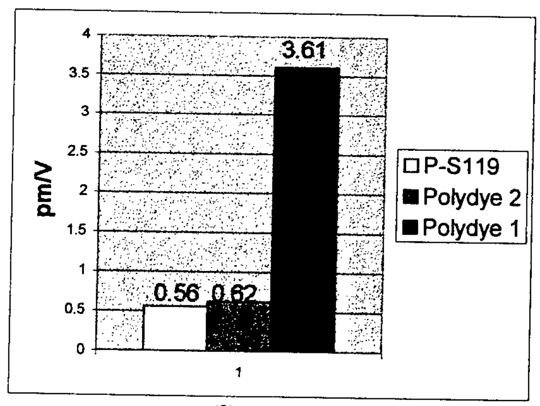


Figure 4-18. $\chi^{(2)}$ Comparison Between New Polymer Dye Materials and Commercially Available Dyes.

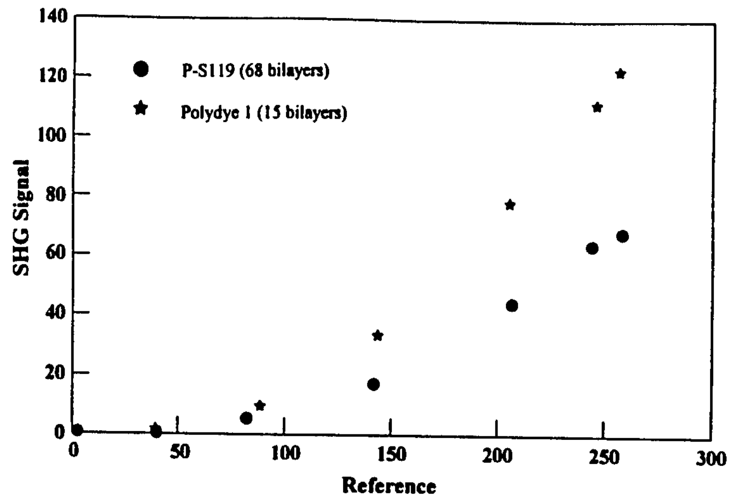


Figure 4-19. Second Harmonic Generation Results of Polydye 1/PDDA ISAM Thin-Films.

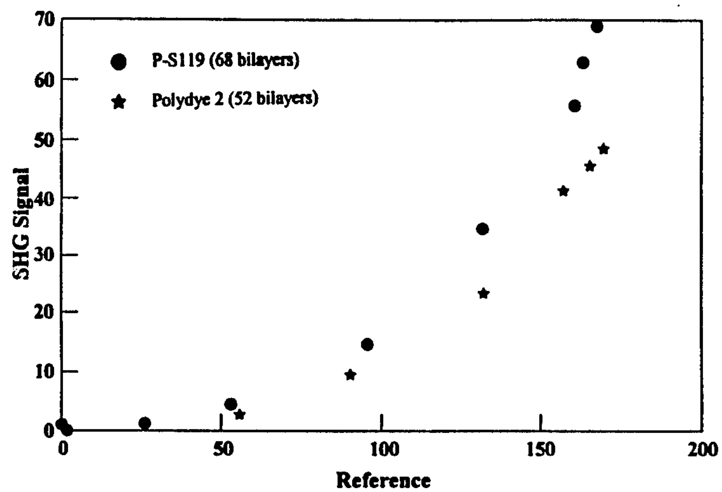


Figure 4-20. Second Harmonic Generation Results of Polydye 2/PDDA ISAM Thin-Films.

4.6 Demonstration of p-n Junction Device Behavior

Previously reported accomplishments in this area include the following.

- Synthesized poly(1,4-phenylenevinylene) (PPV) anionic and cationic precursor solutions; synthesized and characterized ionic self-assembled PPV thin-films
- Synthesized polyhydroxylated fullerene derivative

F&S is currently constructing a p-n junction device using ISAM thin film technology. The *p*-type layer consists of an ionically self-assembled poly(1,4-phenylenevinylene) (PPV) thin-film; a layer of C_{60}, spincoated over the thermally conjugated PPV (see Section 4.3.2) forms the *n*-type layer. A solution of C_{60}/toluene is being prepared for the spincoating step. Aluminium electrodes will be deposited with the Edwards system and the I/V characteristic of the device examined; the device should exhibit rectifying characteristics.

We are currently studying the synthesis of water soluble polyfunctional C_{60} to be ionically self-assembled on top of the PPV thin-film, creating an entirely ISAM device. In addition, other *p*-type polymers and electrode materials are being considered for use in Phase II.

4.7 Demonstration of Electro-Optic Modulation Effect in ISAM Thin-Films

During this Phase I program F&S has demonstrated both ISAM-processed electro-optic thin-film waveguiding and electro-optic modulation in a polar self-assembled prototype device. The simple electro-optic modulator device demonstration article and test geometry shown in Figure 4-21 was discussed in a prior report. This demonstration is important to the development of ISAM-synthesized signal processing devices. We anticipate modulation capability exceeding 20 MHz in ISAM-formed devices, based on the results of similar tests with spin-coated electro-optic modulator devices. Improvements may be possible over such devices due to the increased ability to control homogeneity, thickness and multi-layer functionality.

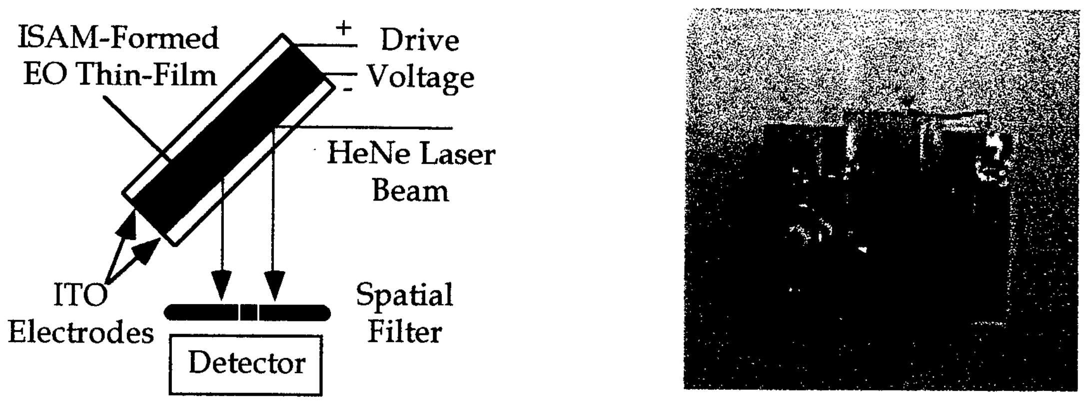


Figure 4-21. Prototype Self-Assembled Electro-Optic Modulator and Test System (left) Demonstrates Feasibility of Prototype Electric Field-Tunable Electronic Device (right).

4.8 Conducting Electrodes and Electrode and Film Patterning

Accomplishments reported in prior reports include the following.

- Designed electrode geometry for first-generation self-assembled PPV LED
- Demonstrated initial electrode pattering on prototype ISAM thin-film devices

The fabrication of patterned thin-films is essential for many electronic and optoelectronic devices. While patterning methods for semiconductors and metals are well established, organic polymer patterning technologies are still in their infancy. A number of methods for fabricating patterned ISAM films were considered during this program, including mechanical [13], lithographic [14] and micromolding [15] techniques. A "charge stamping" procedure [16] appears to offer the greatest advantage for ISAM technology, maintaining the simplicity and low

cost of ISAM processing. The basic concept is to pattern the substrate surface reactivity, and therefore self-assemble films only onto specific regions of the substrate.

The results of F&S' initial attempt at surface reactivity patterning are shown in Figure 4-22. A PDDA/ poly R-478 film was self-assembled onto two patterned glass substrates. After modifying the entire substrate surface using a 30:70 mixture of hydrogen peroxide (H_2O_2) and concentrated sulfuric acid (H_2SO_4), an area corresponding to a negative of the desired film pattern was coated with acrylic, blocking the surface charges to prevent self-assembly. The same procedure should be able to be repeated using higher resolution patterns.

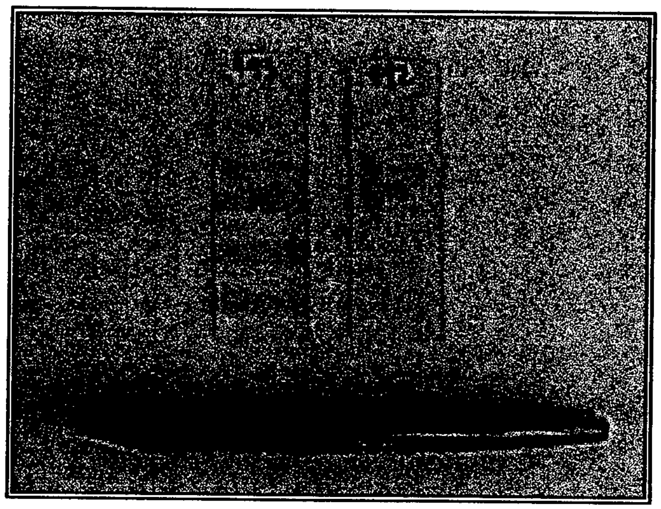


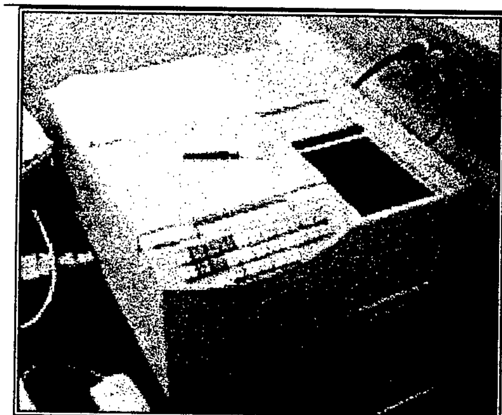
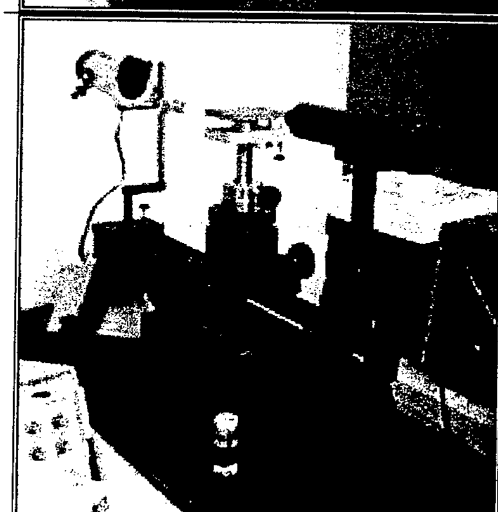
Figure 4-22. Patterned PDDA/Poly R-478 ISAM Thin-Films.

5.0 Discussion of Equipment and Logistics

This section briefly describes new equipment and F&S company logistics important to the success of the current Phase I program.

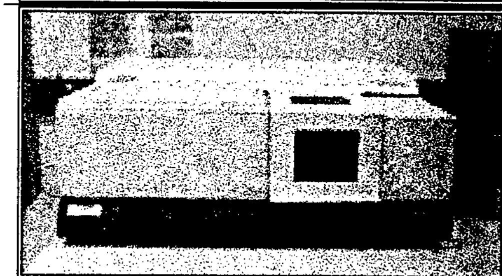
5.1 New Equipment and Importance to Program

New equipment for the fabrication and characterization of both inorganic nanoparticles and ISAM nanoparticle/polymer thin-films has been obtained by the research team during this Phase I program and is shown in the table below.

	Hitachi U-2001 Spectrophotometer • Characterization of UV-Vis absorbance characteristics of solutions and thin-films
	Hitachi F-4500 Fluorescence Spectrophotometer • Fluorescence characterization of optically active thin-film materials
	Rame-Hart Contact Angle Goniometer • Measurement of the water contact angle on the outermost film surface

Rudolph Research Ellipsometer

- Measurement of thickness and refractive index

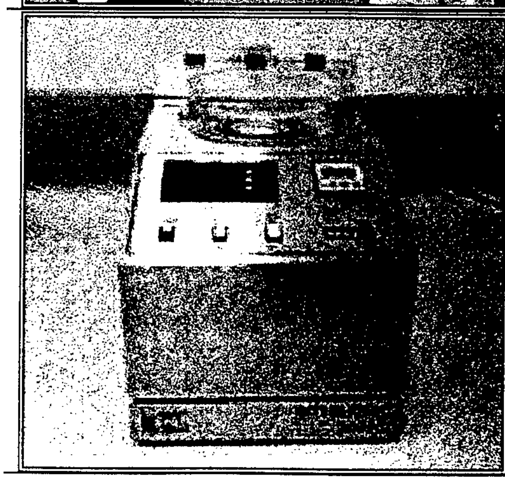


BioRad FTS 6000 FTIR Spectrometer

- Characterization both powder and liquid samples

Edwards Evaporation and Sputtering System

- Fabrication of device electrode coatings and coatings prior to SEM and conductivity analysis



International Crystal Laboratories Roto-Film Spincoating System

- Production of thicker films for comparison and in combination with ISAM thin-films

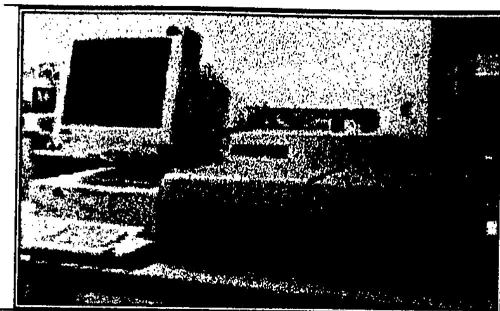
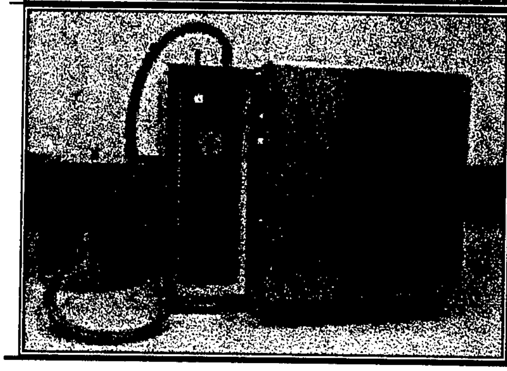
	Malvern Instruments Zetasizer 3000 • Investigation of particle size and distribution
	VWR Scientific Vacuum Oven • Conversion of precursor ISAM films to polymers

Table 5-1. New Characterization Equipment for Nanoparticles and ISAM Thin-Films.

An automated dipping machine should be delivered and available for rapid ISAM sample fabrication in November. Much of this equipment has been purchased on campus at Virginia Tech through an Army Research Office DURIP program monitored by Dr. John Prater.

5.2 New F&S Nanoparticle Coating, Material and Device Manufacturing Space

During this 6-month Phase I SBIR, F&S has expanded its manufacturing facility to include a new 2,000 square foot ISAM processing area; this area is completed and ready for use. Partial financial support for this new facility has been made available through commercialization funding from Fiber Core Technologies (FCT). FCT has worked with F&S on the commercialization of its off-the-shelf line of optical fiber sensors and instrumentation systems.

5.3 Relationship to of This Program to Other Programs

This BMDO Phase I SBIR Program is directly related to other current programs in which the team members are involved. F&S has a separate BMDO Phase I program, monitored by Dr. John Pazik at ONR, involving the development of ISAM-processed protective coatings. F&S is also working on a separate AFOSR Phase I SBIR, monitored by Dr. Charles Lee, for the development of NLO materials and devices through the ionic self-assembly of noncentrosymmetric molecular structures. These three SBIR programs share basic ISAM processing methods and measurement tools, although nanoparticle materials and commercial product applications are different.

F&S is in the process of negotiating a Phase I SBIR program with the Department of Transportation. This program will involve the development and commercialization of ISAM-fabricated protective coatings for large-scale civilian infrastructure, and infrastructure materials incorporating high-

performance nanoparticles. The anticipated overlap between the current BMDO program and this DoT program should be minimal and confined to developments of basic ISAM process chemistry.

F&S also is in the process of negotiating a Phase I SBIR program with DARPA. This program will involve the development and commercialization of frequency-tunable dielectric materials that may be used in RF and microwave devices and systems. Near-term demonstration articles will include discrete tunable capacitors for RF filters and distributed tunable transmission lines for tunable feed and antenna systems.

FEORC at Virginia Tech also has support through a DURIP equipment program from the Army Research Office for the acquisition of nanoparticle synthesis and characterization equipment as indicated above. Virginia Tech has provided 1:1 cash cost sharing for that program. Dr. John Prater in the Materials Division at ARO monitors the program.

6.0 Discussion of Product Commercialization Plan

During the Phase I program, F&S has analyzed the commercial markets that may be available for entry by ISAM-based microelectronic and optoelectronic materials and devices. Details concerning that market analysis have been considered as part of prior reports. This market analysis has been performed in parallel with our technical program, understanding that F&S' ability to commercialize materials and devices is dependent upon both our capability to fabricate devices that meet specific product specifications, and our capability to enter the commercial markets for such products.

F&S' conclusions concerning the microelectronic and optoelectronic markets that may be addressed using ISAM technology are as follows. Significant technical progress has been made in the area of ISAM-processed light emitting devices and optical fiber polarizers, and to a lesser extent polymer *p-n* junction devices and other early active material prototypes. Of these, the commercial market for light emitting devices and displays is by far the largest, exceeding tens of billions of dollars annually. By comparison the commercial market for optical fiber polarizers, isolators and circulators is on the order of hundreds of millions of dollars.

As will be described in the Phase II proposal, F&S will build on its rapid development of ISAM-based light emitting devices to quickly enter the polymer LED and low-end display device market. Technical development progress during the first year of the Phase II program is anticipated to yield demonstration product prototypes of such devices which will be used to leverage large additional investor capital which will be used to develop more complex multi-element displays and systems. This work will also extend our initial demonstration of *p-n* devices, and we anticipate incorporation of such *p-n* structures in future products. At the same time, we recognize the good commercialization opportunity in the area of optical fiber devices, especially with commercialization partner Litton Poly-Scientific, and potential involvement with the large and aggressive 3M optical fiber products group, Alcatel in France, and other companies. As proposed for the Phase II effort, we plan to move these lower-priority products into prototype production, using the equipment and infrastructure developed to first manufacture ISAM-based light emitting devices.

During the Phase I program, we have had commercialization partnering discussions with many companies, and these discussions have been described in part in prior reports. In the Phase II

proposal, we anticipate including letters of support and acknowledgment from several of these companies with which F&S anticipates working cooperatively to develop products, to to whom F&S anticipates selling products in the near-term. These companies include Dominion Semiconductor (IBM/Toshiba), Lockheed-Martin, 3M, Litton, TACAN, Alcatel and others.

7.0 Plans for Next Reporting Period

The current Phase I BMDO SBIR program ends on 31 October 1997. F&S has informed BMDO that it plans to submit a Phase II proposal. This proposal will be submitted to BMDO in the near future.

8.0 References and Bibliography

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9.0 Publications and Presentations

The following are recent or current publications or presentations by the research team concerning the ISAM processing of nanoparticle thin-films.

Recent Publications

1. "Molecular Self-Assembly of TiO_2/Polymer Nanocomposite Films," Y. Liu, A. Wang and R.O. Claus, *J. Phys. Chem. B* 1997, 101, p. 1385-1388, February 1997.
2. "Ionic Self-Assembled Monolayer Multi-Layer Thin-Films," Y. Liu, A. Wang and R.O. Claus, Proceedings SPIE Smart Structures & Materials Conference, San Diego,
3. "Layer-by-Layer Electrostatic Assembly of Nanoscale Fe_3O_4 Particles and Polyimide on Silicon and Silica Surfaces," Y. Liu, A. Wang and R. Claus, Proc. MRS Meeting, San Francisco, March 1997.
4. "Blue Light Emitting Nanosized TiO2 Colloids," Y. Liu and R. O. Claus, *J. Am Chem. Soc.*, vol. 30, no. 22, May 1997.
5. "Metallic and Ceramic Nanocomposites with Ionic Self-Assembled Nanoparticle Coatings," R. Claus, Y. Liu and K. Murphy, Proc. 4th Intl. Conf. on Composites Engineering (Kona, Hawaii), July 1997.
6. "Second Order Nonlinear Optical Thin Films Fabricated from Ionically Self-Assembled Monolayers," J. R. Heflin, Y. Liu, C. Figura, D. Marciu and R. Claus, SPIE Annual Meeting (San Diego), August 1997.
7. "Self-Assembled Nanoparticle-Based Multi-Layer Thin-Films and Devices," Y. Liu, J. R. Heflin, W. Zhou and R. Claus, Proc. ARO Smart Materials Workshop, Blacksburg, August 1997.
8. "Noncentrosymmetric Ionically Self-Assembled Thin Films for Second Order Nonlinear Optics," J. R. Heflin, Y. Liu and R.O. Claus, submitted to OSA Thin-Films Conference, Long Beach, CA, September 1997.
9. "Layer-by-layer electrostatic self-assembly of nanoscale Fe_3O_4 particles and polyimide precursor on silicon and silica surfaces," Y. Liu, A. Wang and R.O. Claus, *Appl. Phys. Lett. 71* (16), 20 October 1997.

Publications and Presentations Pending

10. "Self-Assembled Nanoparticle-Based Thin-Film Materials and Devices," R. Claus, seminar to be organized by Dr. Janet Sater, Institute for Defense Analyses (Alexandria, VA), October 1997.
11. "Nanoparticle/Polymer Materials and Devices," Y. Liu and R. Claus, SPIE Smart Structures and Materials Conf., March 1998.

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13. ABSTRACT *(Maximum 200 words)*
Self-assembled multi-layer fabrication technology offers the ability to implement and replicate a wide variety of cost-competitive submicron-scale and low-power microelectronic, optoelectronic, and physical transducer devices for uses in military and consumer communication, instrumentation and display systems. Ionic self-assembled monolayer (ISAM) techniques for the fabrication of multi-layer nanoparticle/polymer structures offer low manufacturing costs, advantages of processing at ambient temperature and pressure, ability to produce devices on a variety of substrate materials, and broad multifunctional tailoring of materials response through the selective incorporation and long-range ordering of specific organic and inorganic molecules. F&S has modified the ISAM process to incorporate judiciously selected inorganic nanoparticles and organic polymers to form multi-layer thin-films having enhanced electronic, optical, magnetic and other functionalities. Due to ultrasmall nanoparticle size and tight size distribution control, multiple quantum size effects have been demonstrated in such systems for the first time, suggesting the ability to control electronic material properties. F&S has also shown that ISAM processing inherently results in the spontaneous regular geometric ordering of noncentrosymmetric thin-film structures that display ferroelectric-like behavior, and nonlinear optical (NLO), electro-optic, piezoelectric and other responses, also for the first time.

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